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PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Ethylene-Vinyl Ester Copolymers as Pour Depressants for Distillate Fuels

We, ESSO RESEARCH AND ENGINEERING COMPANY, a Corporation duly organized and existing under the laws of the State of Delaware, United States of America, having an office at Elizabeth, New Jersey, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention is concerned with improving the low temperature flow and pour point characteristics of middle distillates. More particularly, the present invention relates to the preparation of improved low cold test hydrocarbon fuels, in particular heating oils and diesel fuels, kerosene, aviation jet fuels and other fuels that are subject to low temperatures. In accordance with the present invention improved middle distillate fuel compositions of improved pour point are produced by using in conjunction with middle distillates a pour depressant comprising a copolymer of ethylene and a vinyl ester of a neo-acid.

With the increase in the use of the full gamut of hydrocarbon fuels, a serious problem has arisen relative to the cold test characteristics of fuels especially in geographical areas frequently subjected to low temperatures. Particularly serious problems have been encountered by heating oils and diesel and jet fuels that have too high a pour point, resulting either in distributional or operating difficulties or both. For example, the distribution of heating oils by pumping or syphoning is rendered difficult or impossible at temperatures around or below the pour point of the oil. Furthermore, the flow of the oil at such temperatures through the filters cannot be maintained, leading to the failure of the equipment to operate.

[P.]

The low temperature properties of petroleum distillate fuels boiling in the range between 250° and 800°F, have also attracted increasing attention in recent years because of the growth of markets for such fuels in subarctic areas and because of the development of turbo-jet aircraft capable of operating at altitudes where temperatures of —50°F. or lower may be encountered.

It is, of course, well-known to add pour depressants to lubricating oils to lower the pour point. These lube oil additives, mostly high molecular weight organic compositions formed by alkylation of benzene or naphthalene or derivatives thereof or by polymerization of lower molecular weight methacrylates, or by condensation-polymerization of various kinds, are not satisfactory in service with middle distillate and lighter fuels. Poor performance of these additives might possibly result from the structural differences between waxes occurring in lubricating oils and so-called middle distillates.

A wide variety of compounds have been found to be effective as pour point depressants for lubricating oil. Among the best known are those prepared either by condensing aromatic compounds with long chain paraffins, such as chlorinated wax, or by polymerizing olefinic esters. It is generally considered that these pour depressants are effective in that in cooling an additive-containing oil, the hydrocarbon chain of the additive becomes incorporated into the crystal lattice of the separated wax, while the other part of the pour depressant molecule prevents the crystals from adhering together to form a gel structure. The failure of these additives to be effective in middle distillates may at least in part be due to the basic difference in the composition between the wax in lubricating oils and that in middle distillate fuels.

It was also considered well-known that the presence of straight or at least nearly straight chains is essential for high molecular weight compounds to be effective as pour depressants for distillate fuels or lubricating oils. Thus, a large number of naphthalene, benzene or phenol condensates with chlorinated waxes have been disclosed in the prior art as pour depressants. Similarly, polymers of unsaturated fatty acid esters or their copolymers with olefins; e.g., with ethylene, have been found effective for this purpose. Generally, the structural requirements of the pour point depressants investigated showed the necessity for an alkyl side chain of at least 12 carbon atoms and a degree of polymerization that gave a solubility corresponding to that of the wax in the oil were essential. See, for example, "Petroleum Refining with Chemicals", Kalichevsky et al, Elsevier Publishing Co. (1956).

The petroleum distillate fuels of the present invention preferably boil in the range of from 250° to 800°F, or more particularly between 350° and 650°F and include heating oils, diesel fuel oils, kerosenes and jet fuels. Aviation turbo-jet fuels in which the polymers may be used normally boil between 250° and 550°F. Kerosenes and heating oils will normally have boiling ranges between 300° and 750°F, and are more fully described in ASTM Specification D-396-48T and supplements thereto, where they are referred to as No. 1 and No. 2 fuel oils. Diesel fuels in which the polymers may be employed are described in detail in ASTM Specification D-975-53T and later versions of the same specification.

Surprisingly, it has been found that contrary to the past teachings, copolymers of vinyl esters of highly branched acids, i.e. acids having methyl and higher carbon number branching at least every eighth carbon atom and as much as every second carbon atom in the acid chain, with ethylene are also highly effective as pour depressants for distillate fuels. Characteristically, however, such copolymers show substantially no potency whatsoever as pour depressants for lubricating oils. The usual method of preparation of such vinyl esters is by reacting a highly branched acid with acetylene. Another way of preparing such esters is that of ester interchange between vinyl acetate and a highly branched acid in the presence of a mercuric sulfate catalyst.

The polymeric pour depressants may, in accordance with the invention, be employed in conjunction with a variety of other additives commonly used in fuels such as those set forth above. Typical of such additives are rust inhibitors, anti-emulsifying agents, corrosion inhibitors, anti-oxidants, dispersants, dyes, dye stabilizers, haze inhibitors, anti-static agents and the like. It will frequently

be found convenient to prepare additive concentrates for use in the various types of fuels and thus add all of the additives simultaneously.

The pour depressants of the present invention comprise a copolymer of ethylene and a vinyl ester of a neo-acid. The proportion by weight of ethylene units in the copolymer must be in the range of from 50—99% by weight and the proportion of vinyl ester units in the range of from 50 to 1% by weight. A very desirable ethylene-vinyl ester copolymer contains 30 to 50% by weight of vinyl ester units, as for example, about 40% parts by weight of vinyl neo-decanoate units.

The molecular weights of the ethylene-vinyl ester copolymer are critical and should be in the range of from 1,000 to 3,500, preferably in the range from 1000 to 3000, e.g. 1,500 to 3,000. The molecular weights are determined by K. Rast's method (Ber. 55, 1051, 3727 (1922)).

The ethylene-vinyl ester of neo-acid copolymer as described above is added as a minor proportion by weight and preferably is used in a concentration in the range of from .002 to .2 by weight, particularly, in a concentration in the range of from .01 to .05% by weight.

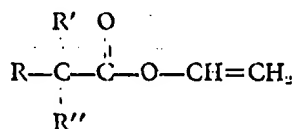
Surprisingly, these low molecular weight copolymers have no effect upon the pour points of lubricating oils, thus emphasizing the difference in structure between the wax associated on the one hand with lube oils and on the other with middle distillates. The low molecular weight copolymers may be prepared by any peroxide process. In some instances, it may be desirable to first prepare a higher average molecular weight copolymerization product and then recover from that product material having a molecular weight within the range between 1,000 and 3,500. Since such copolymerization products normally consist of a spread of copolymers whose molecular weight vary over a wide range, an effective method for recovering the 1,500 to 3,500 molecular weight portion therefrom is to extract the product with a solvent such as normal heptane or methyl-ethyl ketone. Other methods for obtaining the low molecular weight materials include thermal degradation of the high molecular weight polymer or treatment of the high molecular weight copolymer with ozone in order to break the polymer chains.

A very desirable method is to conduct copolymerization in a benzene solution using di-tertiary-butyl-peroxide as initiator at a temperature in the range of 260° to 400°F. The preferred temperature is in the range from 290°F. to 325°F. as for example about 300°F. The pressure is preferably in the range from 600 to 1500 pounds, preferably 800 to 1000 pounds such as 900 pounds. The autoclave or similar equipment contain-

ing the solvent, initiator and branched vinyl ester, e.g. vinyl neo-decanoate, is purged about three times with nitrogen, twice with ethylene and then charged with a sufficient amount of ethylene to yield the desired pressure when heated to the reaction temperature. During the copolymerization, additional ethylene is added whenever the pressure drops by about 100 psig. Copolymerization is considered complete when there is less than a 50 psig pressure drop per hour. The product is stripped free of solvent and unreacted vinyl neo-decanoate under vacuum.

In general, the class of depressants comprise a copolymer of ethylene and a vinyl ester of a neo-acid. The preferred vinyl esters comprise the vinyl ester of neo-decanoic acids.

The present invention evidences surprisingly effective pour depressants prepared from the branched carboxylic acids, broadly referred to above. Specifically, illustrative of the branched carboxylic acids suitable for use in the present invention are those produced from olefins, carbon monoxide and water in the presence of acidic catalysts. These acids can be produced directly from the foregoing reactants, that is, in a one-step process. An alternative to the one-step method is a reaction carried out in two steps; in the first step, the olefin and carbon monoxide are reacted in the presence of an acidic catalyst, essentially in the absence of water, to form an intermediate, hydrolysable reaction product which is thereafter hydrolysed in the second stage to liberate the desired carboxylic acid product and the acidic catalysts. Such branched carboxylic acid products which preferably contain 5 to 20 carbon atoms may then be reacted in accordance with the conditions set forth hereinbefore to produce the vinyl neo-acid ester monomers of this invention which have the following structural formula:



wherein R, R' and R'' represent a substituted or unsubstituted alkyl group each of which can contain from 1 to 10 carbon atoms. Moreover, R, R' and R'' may be similar or dissimilar and may themselves be linear or nonlinear, e.g., they may contain side chains such as methyl, ethyl, or butyl. Thus, the ester monomer of this invention may contain a total of from 7 to 34 carbon atoms. It is preferred, however, that the vinyl ester contains from 10 to 20, e.g. from 10 to 18 carbon atoms. Representative examples of suitable vinyl esters or neo-acids include vinyl 2,2-dimethyl propionate; vinyl 2,2-dimethylbutyrate; vinyl 2-ethyl-2-propyl-

valerate; vinyl 2-methyl-2-butyl-caproate; vinyl 2,2,4-trimethylheptylate; vinyl 2,2,4,6,8-pentamethylpelargonate; vinyl 2-propyl-2,4,6,8-tetramethylpelargonate; vinyl 2,2-dihexyl-4,6,8-trimethylpelargonate; vinyl 2,2-dimethyldecanoate; vinyl 2,2,4,6,8-pentamethyldecanoate; vinyl 2,2-dimethyl-4-ethyldecanoate; vinyl 2-propyl 2-hexyldecanoate; the like and mixtures thereof.

There are many alternative methods available to obtain the highly branched acids to which the present invention is directed. However, simplest and economically most attractive, is that of polymerizing a low molecular weight olefin over a suitable catalyst, such as phosphoric acid, and then reacting highly branched olefins obtained in this fashion with carbon monoxide. The common characteristic of such acids is the absence of hydrogen attached to the carbon atom in α -position in respect to carboxyl group.

Surprisingly the esters of such acids show an exceptional resistance to hydrolysis. Thus, to illustrate their chemical stability, their alkaline hydrolysis proceeds at a rate one hundred times slower than that of ethyl acetate.

Described below are examples of the preparation of polymeric pour depressants from ethylene and a vinyl neo-decanoate which was prepared in accordance with well-known techniques from propylene and carbon monoxide.

EXAMPLE 1

After flushing a one gallon autoclave reactor first with nitrogen and then with ethylene, 1200 grams of benzene and 70 grams of vinyl neo-decanoate were pumped into the reactor which was then heated to 295°F. and the ethylene pressure was raised and maintained during the entire period of the reaction at 950 psig. During the reaction which was carried over 1½ hours, 550 grams of additional vinyl neo-decanoate were charged into the reactor. Also charged in this period were 24 grams of di-tert-butyl peroxide. After 1½ hours, the reactor contents were discharged from the reactor, stripped of solvent and unconverted ester. Ultimately, 704 grams of polymeric material was obtained.

This copolymer of ethylene and vinyl neo-decanoate when added in 0.1 wt. % concentration to a distillate fuel boiling in 350°—650°F. range (ASTM), lowered its ASTM pour point from 20°F. to below -65°F.

EXAMPLE 2

The reaction described in Example 1 was repeated except that 275 grams rather than 550 grams of vinylneo-decanoate were charged into the reactor. Ultimately, 470 grams of the copolymer were received. Again, 0.1 wt. % of this copolymer lowered the

ASTM pour point of the oil described in Example 1 to below -60°F .

EXAMPLE 3

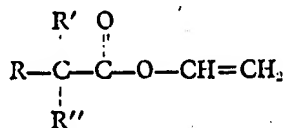
- 5 An ethylene-vinyl neo-acid ester copolymer is prepared in a manner similar to Examples 1 and 2 except that vinyl neo-hexanoate is charged to the reactor. The ASTM pour point of the base oil is favorably affected by this copolymer.

EXAMPLE 4

- 10 An ethylene-vinyl neo-acid ester copolymer is prepared in a manner similar to Examples 1 and 2 except that vinyl neo-octadecanoate is charged to the reactor. The ASTM pour point of the base is favorably affected by this copolymer.

WHAT WE CLAIM IS:—

1. A fuel composition comprising a major proportion by weight of a petroleum distillate fuel and a minor proportion by weight of an oil-soluble copolymer having a molecular weight of between 1,000 and 3,500, said copolymer being a copolymer of ethylene with from 1 to 50 wt.% by weight based on the total weight of copolymer of a vinyl ester of a neo-acid having the following structural formula:



- 30 wherein R, R' and R'' represent a C_1-C_{10} alkyl group.

2. A composition as claimed in claim 1 wherein said copolymer contains from 30—50% by weight of said vinyl ester units.

- 35 3. A composition as claimed in either of claims 1 and 2 wherein said vinyl ester of a

neo-acid contains from 10 to 20 carbon atoms.

4. A composition as claimed in any one of the preceding claims where R' and R'' represent methyl.

5. A composition as claimed in any one of the preceding claims where R represents a branched alkyl.

6. A composition as claimed in any one of the preceding claims wherein at least one of the alkyl groups R, R' and R'' is branched.

7. A composition as claimed in any one of the preceding claims wherein the copolymer has a molecular weight of between 1000 and 3000.

8. A composition as claimed in any one of the preceding claims wherein said copolymer has a molecular weight of between 1500 and 3000.

9. A composition as claimed in any one of the preceding claims wherein the petroleum distillate fuel boils between 250° and 800°F .

10. A composition as claimed in claim 9 wherein the distillate fuel boils between 350° and 650°F .

11. A composition as claimed in any one of the preceding claims wherein the neo-acid contains between 5 and 20 carbon atoms per molecule.

12. A composition as claimed in claim 11 wherein said vinyl ester is vinyl neo-decanoate.

13. A composition as claimed in any one of the preceding claims wherein said copolymer is present in a concentration between 0.002% and 0.2% by weight based on the total weight of the composition.

14. A composition as claimed in claim 1 substantially as hereinbefore described with reference to the Examples.

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